

REMARKS

Claims 1 through 17 are cancelled without prejudice. Now pending are new claims 18-35. The new claims correspond to the cancelled claims and are designed to provide claims of the standard U.S. format. No new matter has been added.

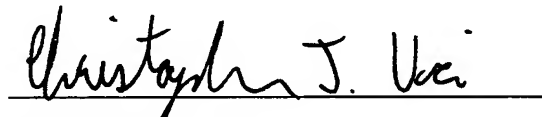
Applicants have provided a substitute specification given the large number of amendments needed to bring the specification into standard U.S. format. Clean and redline versions of the substitute specification have been provided, as has a copy of the original English translation and the original publication of the international application (WO03/103932) and the German application (DE10224981.4). Please utilize the clean substitute specification for any publications.

It is believed that all of the claims are in form for allowance and immediate. Examination of the pending claims and allowance of the same are respectfully requested at this time. If the Examiner has any questions regarding the present application, the Examiner is requested to contact the undersigned at (248) 292-2920.

If for some reason Applicants have not requested a sufficient extension and/or have not paid a sufficient fee for this response and/or for the extension necessary to prevent the abandonment of this application, please consider this as a request for an extension for the required time period and/or authorization to charge our Deposit Account No. 50-1097 for any fee which may be due.

Respectfully submitted,

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(Redline version of substitute specification)

Process for a Layer-By-Layer Configuration of Patterns

**Claim of Priority**

**[0001]** The present application claims the benefit of the filing date of international Application Serial No. PCT/DE03/01636, filed May 20, 2003 (published as WO03/103932, which in turn claims the benefits of German application DE10224981.4, filed June 5, 2002, the contents of which are hereby incorporated by reference in their entirety.

**Technical Field**

**[0002]** The invention as described here refers to a process of layer-by-layer configuration of patterns and/or moulds in accordance with the generic term of the patent claim 4.

**Background**

**[0003]** The application of the rapid prototyping process is well-known as state-of-the-art technology in the production of casting moulds or casting patterns without the use of tools.

**[0004]** A rapid prototyping process to configure casting patterns in particular is already familiar from DE 198 53 834 A1, for example. In this process untreated particulate material, such as quartz sand, is applied on a building platform in a thin layer. Then with the aid of a spray appliance a binding agent is sprayed onto the entire particulate material as thinly as possible. Subsequently a curing agent is applied to selected areas, as a result of which designated areas of the particulate material are solidified. After several repetitions of this process an individually moulded body can be produced from the bonded particulate material. This body is initially embedded in the surrounding unbonded particulate material and can be removed from the bed of particulate material after the construction process has been completed.

**[0005]** If, for example, in this type of rapid prototyping process a quartz sand is used as particulate material and a furan resin as binding agent, with the aid of a sulphurous

acid used as curing agent a casting mould can be produced, which is made of the materials usually used in the mould production process and therefore consists of materials known to the expert.

**[0006]** With such rapid prototyping processes, as already described, first the particulate material, then the binding agent and thereafter the curing agent must be applied. This requires a threefold application of materials for every layer and is therefore very time-consuming.

**[0007]** There have been attempts for quite some time to eliminate at least one coating process to shorten the production time of the pattern.

**[0008]** EP 0 711 213 B1, for example, describes a further rapid prototyping process namely selective laser sintering. In this case the particulate material used is croning sand, that is hot-coated foundry sand with resol or novolack resin. This means that only the particulate material containing resin must be applied and the application of the binding agent is superfluous. Traditional foundry materials can also be used in this process and with these existing casting patterns can be produced from the usual materials familiar to the expert.

**[0009]** However, this production process also has considerable disadvantages. The resin in the sand is not completely hardened during the exposure process. This leads to a reduced so-called green part rigidity of the produced moulds. The desired rigidity is reached only after removal of the loose sand and a subsequent oven process. Apart from the additional process step in the oven there is a high risk of breakage while de-sanding and handling the "green parts". During the oven process an undesired distortion of the components can also occur.

**[0010]** Furthermore croning sands have a relatively high thermic stability, which leads to a poor de-coring capability at the relatively low casting temperatures associated with light alloy casting.

**[0011]** For selective laser sintering croning sands with a higher binder content are also necessary. The consequence of this are larger quantities of gas during the pyrolysis of the binder while casting and therefore a higher reject risk due to blowholes in the component.

**[0012]** Moreover selective laser sintering in general has the disadvantage that the laser is a complex technique and in addition the exposure phase is also relatively time-consuming.

**[0013]** Furthermore only a very limited choice of sand types and grain sizes are available for selective laser sintering, which means that this process is also not very flexible.

**[0014]** A so-called 3D printing process is familiar from the patents US 5,204,055 and also EP 0 431 924 B1. This entails the selective adhesion of particulate material by the addition of binding material. This process has an advantage over selective laser sintering in that it is based on a cost-effective printing technology.

**[0015]** It must be said that, because of the unfavourable material properties, typical traditional foundry binders can be administered only with great technical effort. There is also a danger that the nozzles used to measure out the binding agent become clogged and unusable.

**[0016]** Using a drop dispenser to administer the binding agent makes the mixing of the binder in the component very poor. In order to reach comparable rigidities as with conventionally mixed sands, much higher quantities of binder must be added, which again leads to problems in casting because of the higher quantities of gas.

**[0017]** In PCT/DE00/03324 a further 3D printing process is revealed. This is a selective printing of particles mixed with binder with an activator, to which a gas curing device is connected.

**[0018]** Again it is advantageous that here traditional foundry materials can be used.

**[0019]** However, gas curing is very elaborate for this process. Materials which create a health hazard such as SO<sub>2</sub> are partly necessary, meaning that a very large amount of equipment is required and the safe operation of the apparatus becomes very costly.

**[0020]** As prior to the curing process not even the slightest solidification of the component takes place, slight displacement of the powder bed while layering can lead to the destruction of the entire component.

**[0021]** A further 3D printing process is familiar from DE 197 23 892 A1. This is a selective printing using particles coated with binder, so-called croning sand, with a moderating agent. This is again followed by curing which, according to the disclosure in

ating agent. This is again followed by curing which, according to the disclosure in this publication, takes place by way of radiation. This process also has the advantage of being able to use traditional foundry materials. However, curing of the components is very complex in this process too, because the necessary narrow tolerance in the change of temperature requires an extensive use of equipment.

**[0022]** In the process published in DE 198 53 834 A1, again a 3D printing process, a selective printing of particles sprayed with binder with curing agent takes place. Here too traditional foundry materials can again be used with some degree of flexibility.

**[0023]** The disadvantages of this process include the complex spray application of the binder, inhomogeneous binder mixing and the high concentration of binder in the component.

**[0024]** Moreover, due to the formation of mist in the building chamber caused by the spraying process, a high degree of soiling of the apparatus is consequently caused. As a result an elaborate cleaning of the print head is necessary, as otherwise a hardening of the material on the nozzles occurs and causes its destruction.

**[0025]** Similar disadvantages are illustrated in the selective printing of untreated sand with binding and curing agent, as described in WO 01/72502 A1.

### **Summary of the Invention**

**[0026]** The present invention includes a process to produce models in layers, whereby a first material and then selectively a second material is applied in layers on a building platform and these two application stages are repeated until a desired pattern is achieved. The two materials form a solid if a suitable mixture ratio is used and the first material is a material mixture. The material mixture is at least partially prepared prior to each application stage.

### **Brief Description of the Drawings**

**[0027]** The Figure shows a schematic view of the present invention.

### **Detailed Description of the Invention**

**[0028]** Given this background situation, it is the task of the invention as set out here to make available a process whereby it is possible to carry out layer-by-layer configuration of patterns in the most time-saving and cost-effective manner. Furthermore the process should be able to be used industrially based on its reliability and user-friendliness.

**[0029]** This task is solved by implementing a process for the configuration of patterns in layers, whereby using a building platform, a first material and then selectively a second material are each applied in layers and these two application steps are continually repeated until a desired pattern is achieved. To this end, the two materials form a solid, provided a suitable mixture ratio is used. The first material concerned is a material mix and is at least partially prepared prior to each layer stage.

**[0030]** This process has proved itself to be advantageous, as it means that the processing times of the material mixture can be kept short and therefore the slightly volatile ingredients in the binding agent are retained. The preparation can take place as required during the application process.

**[0031]** It would however also be possible to mix the total necessary amount of material required for the process in advance; very elaborate measures would however have to be taken in order to prevent the vaporization of volatile components in the binder. Indeed, it is this highly elaborate use of equipment that this process intends to avoid.

**[0032]** A further advantage of this so-called "in-process" mixing is also the greater degree of flexibility. Firstly, only so much sand is mixed as is actually required. This means that, should the process be completed early, there will be no unnecessary wastage. If the building process is prolonged by additional loading of components, there is no danger of shortage of material due to the initial predetermined quantity of material. Furthermore the sand and the component materials can even be altered during the process. Therefore, in contrast to the selective laser sintering process, the user does not have to decide at the beginning of the process on a specific type of material for the entire building process.

**[0033]** A further advantage of this process in comparison with selective laser sintering is the use of cost-effective raw materials in contrast to expensive special types of sand.

**[0034]** In accordance with a preferred embodiment of this invention, the material mixture is prepared continually. This means that the mixture is always round about the same "age" and therefore has the same properties in respect of any components etc. which may have evaporated

**[0035]** In accordance with a further preferred embodiment of the invention process, the material mixture is prepared in batches. A continual mixing process, as is usual in conventional moulding processes, would in fact also be possible, but because of the relatively low processing speed during the layer configuration technically complicated.

**[0036]** Preferably the material mixture should consist of a particulate material and a reactive material.

**[0037]** If in the invention process the second material, in accordance with a further preferred embodiment, contains an activator, then bonding of the components at room temperature by way of a chemical reaction can take place.

**[0038]** For this it would be possible for the curing of the bonded material to occur because of a chemical reaction of the materials. Equally, curing through a physical reaction between the materials would also be conceivable.

**[0039]** Preferably with the invention process the repeated layer application and the application of the second material takes place within the time required for solidification of the two materials. Thus a solidification within the surface section and to the layer below and therefore a better layer bonding can be achieved.

**[0040]** Particularly good results could be achieved when, in the preparation of the material mixture, a residual porosity remains, as this is accompanied by an increased gas permeability, which has a favourable effect during casting. Moreover the second material then also reaches deeper-lying particles, which results in better curing.

**[0041]** In accordance with a preferred embodiment of the invention process the second material is applied by means of droplet production technique. This technology has proved itself to be very accurate, reliable and simple.

**[0042]** An application of the second material by using a dispensing technique would, however, also be conceivable.

**[0043]** Particularly good results could be achieved when the second material has a carrying agent which is not involved in the curing agent reaction, as with such a sub-

stance the wetting of the material mixture made up of particulate material and the first reactive components can be adjusted independently of the chemical quantity ratios necessary for reaction.

**[0044]** There is still a desire to be able to process varying layer thicknesses. This also means that the addition of curing agent must be adjusted for each layer and that preferably independently from the chosen dissolution of the curing agent application.

**[0045]** For this reason a non-reacting carrying agent is mixed with the curing agent, with the help of which the required quantity ratio can be adjusted.

**[0046]** Preferably ethanol is used as a carrying agent. However, other alcohols could also be used, even water is a possible alternative. Ethanol is favourable because it is slightly volatile. If possible, however, volatilization of the entire carrying agent should have occurred prior to casting, as it can have a negative effect on the casting. During the process itself a large part of the ethanol already evaporates from layer to layer. The residual amount can be evaporated in a brief oven process (1 h at over 80°C).

**[0047]** Ethanol also has two other positive effects. The viscosity of the agent to be dispensed is a limiting factor with the DOD (drop-on-demand) record heads. With ethanol the viscosity of the curing agent can be reduced, which improves the functioning of the print heads.

**[0048]** Without a diluent a curing agent quantity to be dispensed adapted to the chemical quantity ratio would be so low that a locally severely limited curing process must be assumed. Moreover at this point an excessive addition of curing agent would take place, which would have a negative effect on the chemical reaction and this would in turn have negative effects on the rigidity of the components.

**[0049]** The carrying agent quantity can be calculated mathematically:

**[0050]** Given the desired proportional mass of the curing agent in the particulate material is  $x_h$ , the particulate material weight per layer is  $m_{s,l}$  then the necessary curing agent quantity  $m_h$  is calculated as follows:  $m_h = m_{s,l} \cdot x_h$

**[0051]** Given additionally that the required printing resolution is  $r_p$  in dpi, the volume of the liquid particles is  $v_{f,d}$ , the area of the building surface is  $A_b$ , the density of the curing agent is  $\rho_h$ , then the proportional volume of the carrying agent  $x_l$  can be calculated



$$x_t = \frac{m_h}{\left(\frac{r_p}{0,0254}\right)^2 \cdot v_{f,d} \cdot A_b \cdot \rho_h}$$

**[0052]** If the particulate material used is a moulding sand such as quartz sand, silicate sand, chromite sand, zircon sand, olivine sand, chamotte sand, corundum sand or/and carbon sand, good results can be achieved with the models. Newer materials such as synthetic sands, for example cerabeads, can demonstrate advantages in special applications and can be similarly used. These particulate materials can be used on their own or as a mixture.

**[0053]** Equally it would be conceivable in respect of this invention that the particulate material is made up of a polystyrene powder, a polyamide powder or other polymer particulate materials, or a mixture of these powders.

**[0054]** A furan resin and/or a phenol resin are particularly suitable for the first reactive material.

**[0055]** The components produced in accordance with the invention can be used preferably as moulds for non-ferrous castings or in the production of investment patterns for non-ferrous castings.

**[0056]** In accordance with the invention the particulate material, preferably quartz sand, is mixed with a small proportion of epoxy resin (binder) and in the case of furan and phenol resins with a curing agent in predetermined quantities either in batches or mixed continually and subsequently made into a mould. Typical mixture proportions are between 0.6 and 1.8 weight -% content of resin in the quartz sand.

**[0057]** Conventionally the production of the mould usually takes place in a moulding machine using a pattern to achieve the moulding; production of the mould also partially takes place by hand. The curing, that means the bonding of the sand particles to a firm shape then takes place chemically or physically by curing the binder. The hardening process can be supported by the use of heat.

**[0058]** Once the mould is finished it is then prepared for casting. Usually several mould components such as upper and lower box and cores are assembled. If required the mouldings are then sized. Then the liquid metal is poured into the designated sprue. The high temperature of the heat melting bath leads to cracking of the resin content of

the sand, especially of the outer parts nearest the heat melting bath. The gas which forms during this process is led away via the porosity of the sand to the exterior.

**[0059]** In order to avoid undesired gas cavities, the binder concentration in the mould should be as low as possible. However, the proportion of binder should be adequate enough to guarantee the mechanical stability of the mould, even under the pressure of the metal heat melting bath. Moreover, the particles should be bonded until the metal has cooled down at least on the outer zone, and a so-called casting skin has formed.

**[0060]** After the metal has set, the sand should ideally trickle out of the mould, if possible without the influence of any further heat application or mechanical aids.

**[0061]** The declared aim, therefore, for the production process in layers as envisaged in the invention is to administer as little binder as possible but nevertheless an adequate amount in the particulate material.

**[0062]** Further advantageous variations of the invention as laid out here can be found in the dependent claims and the description as set out below.

**[0063]** To provide a more detailed explanation the invention is described hereafter in more detail by using preferred examples of implementation and by reference to the drawing.

**[0064]** In the drawing the only figure illustrates the pre-mix and supply of the pre-mixed material.

**[0065]** As an example, the invention process and the invention apparatus for use in a layered configuration of casting moulds made of particulate material, in this case foundry sand, binder and curing agent, is to be described hereafter in a rapid prototyping process.

**[0066]** The foundry sand mixed with binder during the application stages is applied on a platform in a thin layer (ca. 0.15 – 0.3 mm layer thickness). During the next stage the curing agent is selectively printed on to predetermined areas of the sand by means of a print head. This need not necessarily be performed this way, but could also be carried out by means of another dosage, as for example by way of a screen printing process or something similar.

**[0067]** Wherever the curing agent penetrates into the sand, a chemical reaction is set off and the particles bond together locally, in fact only on the exact spots where cur-

ing agent was applied. No reaction takes place in the remaining areas, Quartz sand mixed with binder therefore remains unbonded. During the next stage the building platform is lowered corresponding to the amount of the layer thickness and the process consisting of application of the pre-mixed sand and pressing with curing agent on to predetermined areas begins again. This process loop is repeated until the desired construction height has been reached and the component has been completed. This now lies embedded in the uncured sand and only has to be removed from the surrounding sand.

**[0068]** In this example a traditional foundry resin from the family of furan resins is used as a binder. Other resins like, for example, phenol resins or also PU resins could also be used.

**[0069]** The particulate material combined with binder is mixed in batches during the building process. Here care must be taken that the batch is processed as quickly as possible because of the slightly volatile but reactive components in the resin. A large proportion of the resin consists of furfuryl alcohol, which has a very high vapour pressure even at room temperature. In order to avoid an unwanted reduction of these constituents in the resin, attention should be paid to the timely processing of the material.

**[0070]** The quantity of binder can be varied and is preferably in the region of 0.6 – 1.5 weight -% of the untreated particulate material.

**[0071]** The curing agent chosen is a sulphurous acid, as set out in the example described. For an optimum chemical reaction with the binder the proportion of the sulphurous acid should be in accordance with the binder manufacturer's instructions, within a range of between 30 % and 50 weight % of the binder quantity. Given these binder weight proportions this means that ca. 0.18 – 0.75 weight % of the sand should be dosed.

**[0072]** With the invention process the percentage amounts of the curing agent present in the mixture have an influence which cannot be disregarded. If too little curing agent is put on the sand layer previously mixed with binder, the reaction is delayed or, if the quantity falls short of the required minimum, the process will not begin at all.

**[0073]** If, by contrast, too much curing agent is introduced the component may over-cure. In this case too the component produced rapidly loses its rigidity.

**[0074]** Furthermore it is important for the curing agent to reach as many areas of contact of the particle as possible, setting off the chemical reaction with the binder. Also a decisive factor is that the curing agent is well distributed in the particulate material. A localised curing agent overdosage cannot be compensated over the surface and leads to a reduction of the rigidity.

**[0075]** Therefore it is important that the whole desired area is printed by the curing agent in adequate quantities and as evenly as possible.

**[0076]** The quantity of curing agent must therefore be adapted to the layer volume and the binder concentration. A quantity regulation via the DOD print heads is only possible to a limited extent.

**[0077]** With these systems the drop size is in fact relatively rigid as it is determined by the configuration design of the printer. Typically the drop diameter of the curing agent can be selected within a range of 10  $\mu\text{m}$  – ca. 200  $\mu\text{m}$ . In our case the drops have a volume of 180 pl. Moreover the number of drops is determined by the desired resolution. This means that if the amount of curing agent added is adjusted by altering the number of drops, the quality of the produced components, which is to a considerable extent determined by the print resolution, will suffer. In a worse-case scenario the drops must be placed so far from each other that the homogeneity of the curing agent added is no longer sufficient to cure the binder over the total desired surface. The rigidity of the component would be considerably reduced because of this.

**[0078]** The problems associated with the drop size and drop quantity are increased by the desire to be able to process varying layer thicknesses. This also means that the amount of curing agent added has to be adjusted for each layer and this preferably independently of the chosen dissolution.

**[0079]** For this reason a non-reactive carrying agent is mixed with the curing agent, with the aid of which the desired quantity ratios can be more easily adjusted. As in the example described here the non-reactive carrying agent is ethanol.

**[0080]** In the example described here the quantity of carrying agent is calculated as follows:

The quartz sand weight per layer is 315 g;

The proportional mass of the binder in the quartz sand  $x_b$  is 1.0 weight -%;

The proportional mass of the curing agent in the quartz sand  $x_h$  is 0.5 weight -%;  
This results in a calculated curing agent quantity in the layer of 1.58 g;

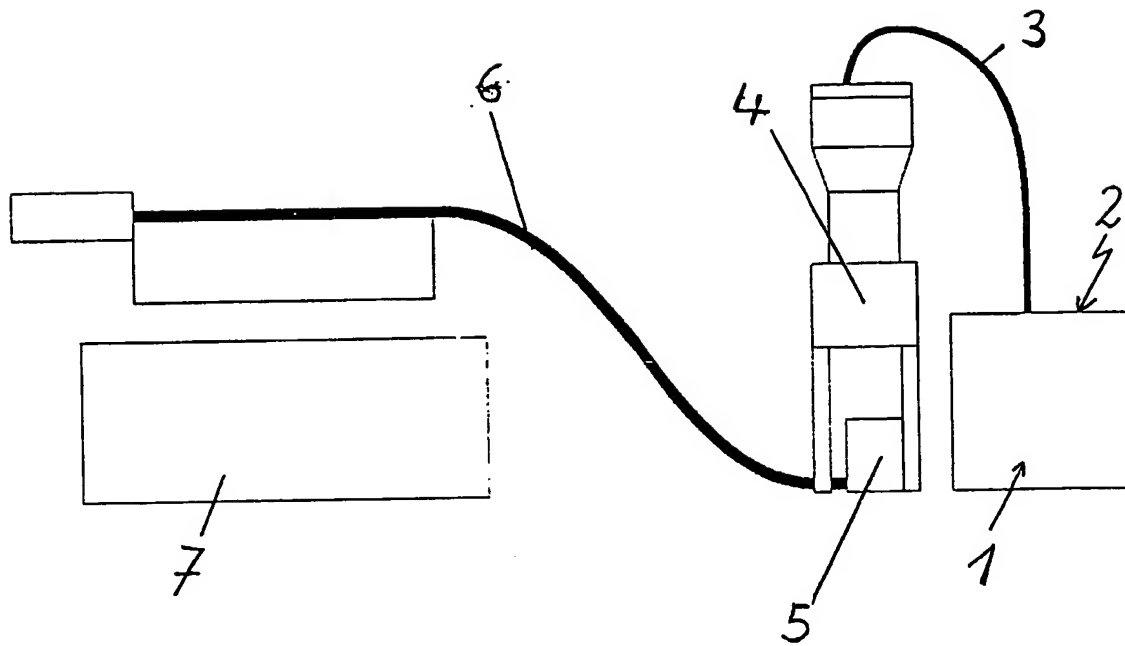
The desired print resolution  $r_p$  is 150 dpi,  
the drop volume  $v_{f,d}$  is 180 pl,  
the area of the building surface  $A_b$  is 1.125 m<sup>2</sup>,  
the density of the curing agent  $\rho_h$  is 1,206 kg / l,  
This results in a proportional volume of the curing agent to the total dosage quantity of 18.5 %.

**[0081]** It is described with reference to the figure how the pre-mixing and the supply of the pre-mixed material to the coating machine in accordance with a preferred embodiment can take place.

**[0082]** As seen in the Figure, for this purpose a specified quantity of untreated particulate material 1 is taken from a so-called big bag 2 and led via a conveyor belt 3, e.g. a pneumatic conveyor, to a mixer 4. This mixer mixes the particulate material 1 in the mixing chamber, e.g. by way of a rotating impeller as per the prescribed mix design with the resin binder and leads the batch received to a so-called receiver tank 5. The receiver tank 5 is fitted with a level sensor and activates the mixing process when underfilled. If in addition there is to be an electromechanical vibrator at the receiver tank, bridging in the quartz sand, which is a frequent problem, can thus be avoided or at least considerably reduced.

**[0083]** The particulate material pre-mixed as described, which is now slightly sticky, is conveyed via a spiral conveyer 6, depending on the requirement of the coater 7 to this piece of equipment.

**[0084]** This described system excels in that it is fully automated and, given the necessary particulate material supply, can be operated without interruption in continuous operation mode.



Figur